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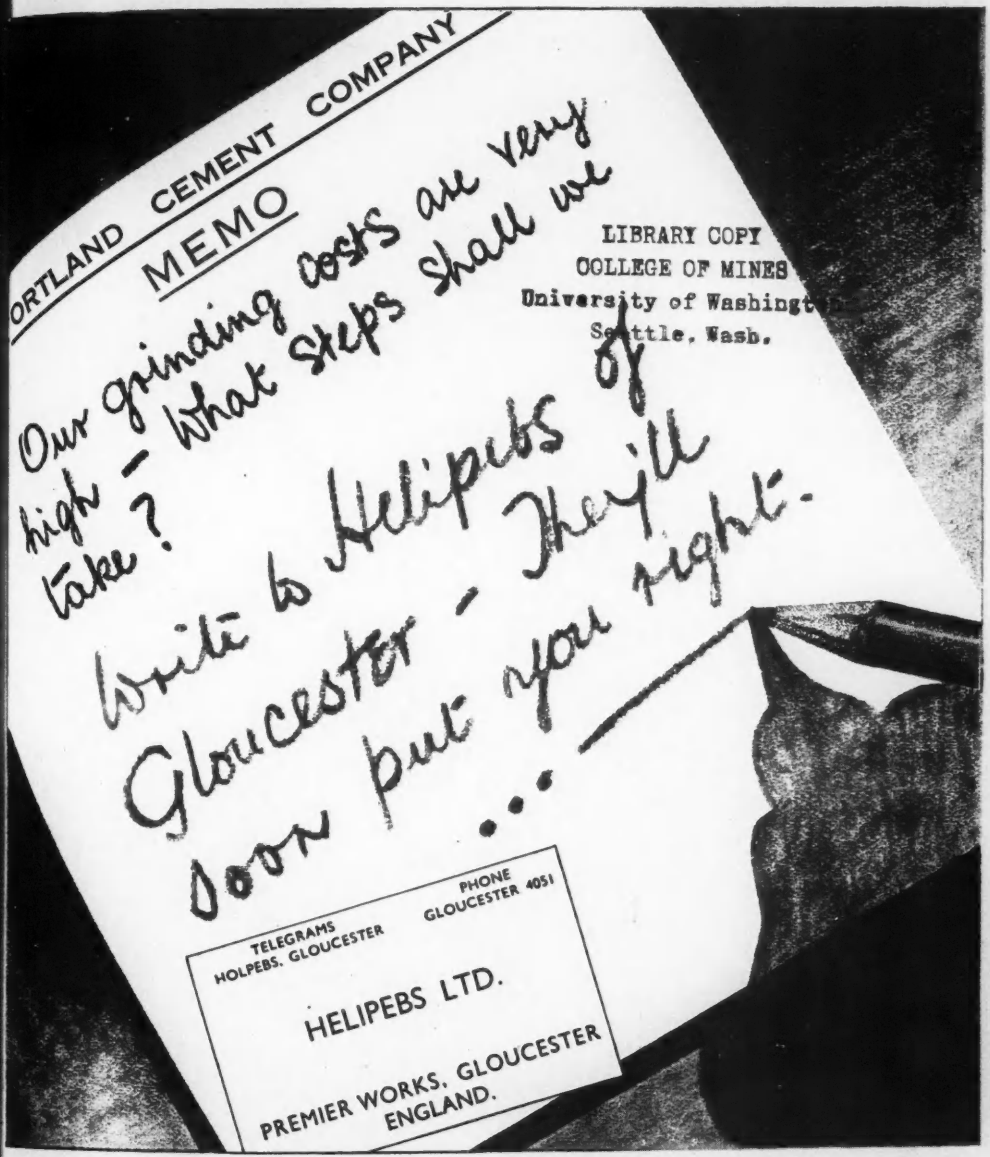

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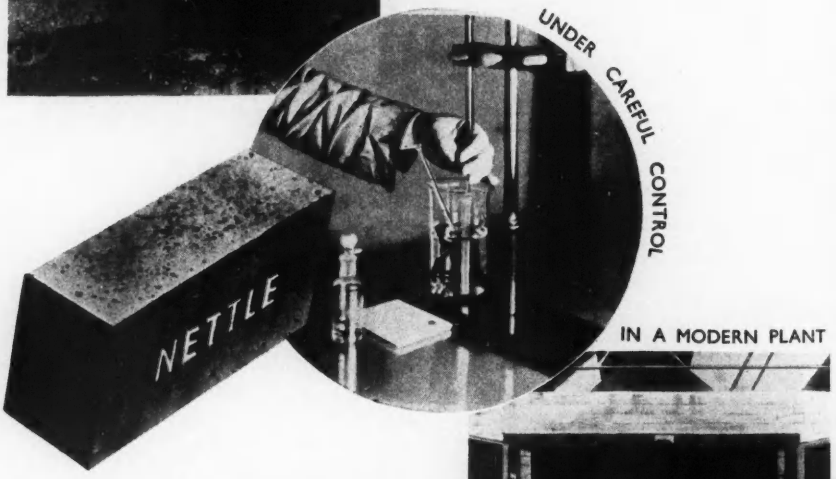

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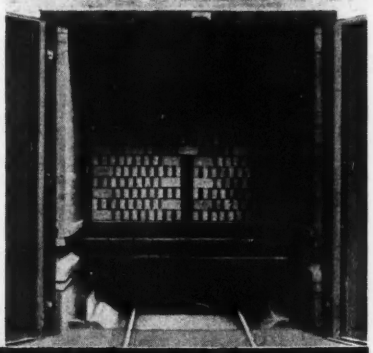

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Proportioning Raw Materials for Cement Manufacture.

In the British Standard Specification for Portland Cement, No. 12—1940, the maximum lime (CaO) permissible in Portland cement is based on the theory of Dr. F. M. Lea and Dr. T. W. Parker.* In this specification " the percentage of CaO (in cement), after deducting CaO necessary to combine with SO_3, shall not be more than 2·8 times the percentage of SiO_2 plus 1·2 times the percentage of Al_2O_3 plus 0·65 times the percentage of Fe_2O_3,"† or

$$\text{Max. CaO } (\%) = 2{\cdot}8\ SiO_2 + 1{\cdot}2\ Al_2O_3\ (\%) + 0{\cdot}65\ Fe_2O_3\ (\%) \qquad (1)$$

It is convenient to express the actual CaO content as a percentage of the maximum CaO permitted by this equation, e.g. if the maximum CaO according to the equation is 69·5 per cent. and the actual is 66 per cent., then the percentage saturation is $\frac{66}{69{\cdot}5} \times 100 = 95$ per cent. If, therefore, it is desired to calculate the analysis of clinker from given raw materials the following procedure may be adopted.

Assume that the analyses of the raw materials (chalk and clay) are as follows :

	Chalk	Clay
	(per cent.)	(per cent.)
SiO_2	0·4	56·3
Al_2O_3	0·2	21·4
Fe_2O_3	0·3	4·5
CaO	54·8	2·4
MgO	0·7	1·6
Loss on ignition ..	43·2	9·4
Alkalis, etc. ..	0·4	4·4
	100·0	100·0

It is necessary to decide on the degree of saturation required in the clinker. It is convenient to take this at 100 per cent. and allow the fuel ash to reduce the CaO

somewhat below the maximum allowed, and this is usually adopted for simplicity. To illustrate the method more generally, suppose that 95 per cent. saturation is desired without allowing for fuel ash, then the constants in equation (1) are :

$$\text{Lime saturation} = 2{\cdot}8 \times \tfrac{95}{100}\text{SiO}_2\,(\%) + 1{\cdot}2 \times \tfrac{95}{100}\text{Al}_2\text{O}_3\,(\%) + 0{\cdot}65 \times \tfrac{95}{100}\text{Fe}_2\text{O}_3$$
$$= 2{\cdot}66\ \text{SiO}_2\,(\%) + 1{\cdot}14\ \text{Al}_2\text{O}_3\,(\%) + 0{\cdot}62\ \text{Fe}_2\text{O}_3\,(\%).$$

The next stage in the calculation is due to the fact that in both the chalk and clay there are quantities of CaO, SiO_2, Al_2O_3, and Fe_2O_3. In both, therefore, there are already certain proportions of potential clinker of the desired lime saturation. The amounts can be calculated as follows :

Chalk		Clay	
SiO_2, $0{\cdot}4 \times 2{\cdot}66$	$=1{\cdot}064$	SiO_2 required for CaO	
Al_2O_3, $0{\cdot}2 \times 1{\cdot}14$	$=0{\cdot}228$	$=2{\cdot}4 \times \frac{1}{2{\cdot}66}$	$=0{\cdot}9$
Fe_2O_3, $0{\cdot}3 \times 0{\cdot}62$	$=0{\cdot}186$	CaO	$=2{\cdot}4$
CaO	$=1{\cdot}478$		
$SiO_2+Al_2O_3+Fe_2O_3$	$=0{\cdot}900$	Potential clinker	$=3{\cdot}3$
Potential clinker	$=2{\cdot}378$		

CaO must now be allocated to the argillaceous material left in the clay after subtracting the amount of SiO_2 required for the potential clinker.

Clay	
SiO_2, $55{\cdot}4 \times 2{\cdot}66$	$=147{\cdot}4$
Al_2O_3, $21{\cdot}4 \times 1{\cdot}14$	$= 24{\cdot}4$
Fe_2O_3, $4{\cdot}5 \times 0{\cdot}62$	$= 2{\cdot}8$
Total CaO required per 100 parts of clay	$=174{\cdot}6$

The amount of CaO required for the potential clinker in the chalk must be subtracted from the CaO content of the chalk. This leaves 53·32 per cent. CaO available in the chalk for combining with the available argillaceous materials in the clay. One hundred parts of clay require 174·6 parts of CaO ; therefore the parts of chalk required for the clay are $\frac{174{\cdot}6}{53{\cdot}32} \times 100 = 327{\cdot}4$. The mixture required is therefore 1 part clay and 3·274 parts chalk.

In order to calculate the amount of clinker obtained from this mixture, the various amounts of SiO_2, Al_2O_3, etc., in the constituents are added together as follows, with the assumption that one-fourth of the total alkali present in the raw material is driven off in the kiln.

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Alkalis, etc.
Clay	56·3	21·4	4·5	2·4	1·6	3·3
Chalk	1·3	0·7	1·0	179·4	2·3	1·0
	57·6	22·1	5·5	181·8	3·9	4·3

This adds up to 275·2, showing that 1 part of clay and 3·274 parts of chalk give 2·752 parts of clinker.

The ash in the coal has still to be accounted for, and this may be done as follows. A typical British coal used for rotary kilns has (say) 10 per cent. of ash of the following composition :

SiO_2	45 per cent.
Al_2O_3	30 ,,
Fe_2O_3	15 ,,
Rest	10 ,,
	100 ,,

The coal consumption may be assumed to be 27 per cent., and it is usual for about 65 per cent. of the ash to be taken up by the clinker, the remaining 35 per cent. going to the dust chamber and the chimney. The amount of ash will therefore be $27 \times 0{\cdot}65 \times 0{\cdot}1 = 1{\cdot}75$ parts per 100 parts of clinker. This may now be added to the constituents of the clinker from the chalk and clay, after multiplying each component of the ash given in the analysis by $0{\cdot}0174 \times 2{\cdot}752 = 0{\cdot}048$.

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Alkali, etc.
Clinker from chalk and clay ..	57·6	22·1	5·5	181·8	3·9	4·3
Ash	2·2	1·4	0·7	—	—	0·5
	59·8	23·5	6·2	181·8	3·9	4·8

This corresponds to 280 parts of clinker including ash, and it is obtained by burning a mixture of 100 parts of clay and 275·2 parts of chalk. Reducing these proportions to a basis of 100 gives the composition of the resultant clinker as follows :

SiO_2	21·4 per cent.
Al_2O_3	8·4 ,,
Fe_2O_3	2·2 ,,
CaO	64·9 ,,
MgO	1·4 ,,
Alkali, etc.	1·7 ,,
	100·0 ,,

From equation (1) the maximum CaO permitted by B.S.S. No. 12–1940 will be found to be 71·3 parts, hence the final CaO saturation is $\frac{64{\cdot}9}{73{\cdot}1} \times 100 = 91$ per cent.

The method described is the most modern procedure in the determination of the proportions of raw materials to use for the production of clinker complying with B.S.S. No. 12–1940. In the earlier editions of the B.S.S. the method was

simpler, as the maximum CaO was indicated by assuming that all the SiO_2 and Al_2O_3 are in the forms $3CaO.SiO_2$ and $3CaO.Al_2O_3$. The lime ratio of the earlier British Standard Specifications was obtained from the molecular formula $\frac{CaO}{SiO_2+Al_2O_3}$ not greater than 3. For the clinker analysis previously given this would therefore be $\frac{64{\cdot}9}{56} \div \left(\frac{21{\cdot}4}{60} + \frac{8{\cdot}4}{102}\right) = 2{\cdot}644$. This older method is naturally more familiar to cement chemists, who will no doubt continue for some time to think in terms of this lime ratio. For such, it may be interesting to note that for nearly all British cements the new lime-saturation figure can be found approximately by multiplying the lime ratio by 34, e.g. for clinker as previously described: lime ratio $= 2{\cdot}644 \times 34 = 90$ per cent. saturation, compared with 91 per cent. actual.

* Lea and Parker. The Quaternary System, $CaO-Al_2O_3-SiO_2-Fe_2O_3$, in relation to Cement Technology. Building Research Technical Paper No. 16, 1935.

† B.S.S. No. 12—1940, Section 9, p. 8.

By-Products from the Manufacture of Lime.

THE possibility of making magnesium from dolomitic lime is dealt with by Mr. N. C. Rockwood in a recent number of " Rock Products," where it is stated that, while the war has added great impetus to the demand, there seems little doubt that magnesium will be used in the future not only for commercial aircraft but for motor cars, railway trains, and many other purposes where lightness and strength are desirable. A number of patents has been issued to the Dow Chemical Co. for alloys of magnesium and silver, calcium, manganese, copper, zinc, tin, cadmium, nickel, barium, etc. With magnesium a common metal, as it now is, we may expect a tremendous development in special alloys for a variety of uses. To a lesser extent the same may be true of the metal calcium in the years to come, when cheap means of reducing the oxide (lime) are achieved.

There is great activity in investigating means of separating the magnesia (MgO) from the calcia (CaO) in dolomitic limes, and using the magnesia for refractories and other commercial purposes. Since magnesite deposits are rare and dolomite deposits common, a feasible process for separating out the magnesia from dolomite, or dolomitic lime, would have broad application.

The American Institute of Mining and Metallurgical Engineers has recently published a paper by Mr. Max Y. Seaton on " Production and Properties of Commercial Magnesias " (Technical Publication No. 1496), where the possibilities of separating magnesia from dolomite are described as follows: " What may well be considered inexhaustible quantities of magnesia occur combined as dolomite. The separation of a relatively pure magnesium oxide from dolomite has long been an intriguing project to the chemical engineer, and a variety of recovery schemes has been explored. Methods based on the difference of hardness between magnesium and calcium oxides after dolomite has been calcined (and in some instances partially hydrated) have been patented, but are believed to

have found no commercial use. Considerable work has been done on the relatively simple scheme of calcining dolomite and leaching it with water to dissolve the lime and leave a relatively pure magnesia. Immense quantities of water are required because of the low solubility of lime, and securing, pre-purifying and disposing of this water presents a real problem. Despite these difficulties, however, this process is being successfully used on a large scale for the production of a relatively high-lime magnesia for refractories. Other processes that have attracted interest include the long-used Pattinson process for the production of basic magnesium carbonate, the sugar-solution method of Scheibler, various processes employing hydrogen sulphide, the calcium chloride cyclic process of Clossen, and numerous other processes. Important quantities of magnesia no doubt will soon be produced in conjunction with the ammonia-soda process for the production of sodium carbonate." Apart from its use as a refractory, Mr. Seaton describes chemical magnesia and activated magnesia. He says " more and more attention has been paid of late to the rate of chemical activity of magnesium oxide. If weak organic acids are being neutralised, or if the magnesia is employed for combined physical and chemical purposes, questions of ultimate crystal size and reaction rate become governingly important." In referring to activated magnesia, he says, " studies of the rate of reactivity of magnesium oxides have led to the discovery that proper processing can develop these oxides in such form that they are intensely active both physically and chemically, serving as splendid selective adsorbents for a variety of organic materials." The field of usefulness of the activated magnesias has been explored in only the most casual fashion. It is believed that in the end some substantial outlets for such materials will be developed." Mr. Rockwood says that nothing, so far as he knows, has been done with activated calcium oxides, but apparently here also is a large field of exploration and development for the lime manufacturer. Enough is already known to predict that the field of lime manufacture has scarcely been explored for the uses of lime as a chemical, and not merely as a crude product in the preparation of other chemicals.

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Developments in Clinker Grinding.

SINCE the year 1936 the clinker grinding department of one of the works of the Medusa Portland Cement Co. has been changed in an endeavour to improve the operation of the plant and to improve the quality of the cement.

In 1936 heat recuperators were put on each kiln to quench the clinker down to about 1000 deg. F. Passage through 6ft. by 60ft. rotary coolers reduced the temperature to about 150 deg. F. for handling by conveyor into the grinding mill feed-bins. Earlier, the rotary coolers discharged clinker at 550 deg. F., a temperature which was too high for immediate grinding. Before 1936 clinker was ground in three 7ft. by 22ft. Compeb mills. Each had a preliminary section 7ft. long followed by 14ft. of length effective as a tube mill, with centre feed and peripheral discharge. The capacity of each mill was 50 barrels of cement per hour, but the surface was only 1425 sq. cm. per gramme. In 1936 an 18ft. mechanical air separator was close-circuited with two of the 7ft. by 22ft. Compeb mills, with an arrangement for the third one to be operated either in open circuit or with the air separator. At that time the compartment grid bars were opened to speed the passage of material through the mills. Separator rejects returned into the mills with the fresh feed. With this system of grinding the capacity of each mill went up to 60 barrels per hour and the surface area was increased. To get this production, a circulating load equivalent to 75 per cent. of the feed was maintained. Feed into the separator comprised 60 barrels per hour of fresh feed plus 45 barrels of rejects.

Then followed complete alteration to increase the specific surface of the cement. One Compeb mill was converted into a preliminary ball mill with double-end feed and common centre discharge. The other two mills were changed to straight tube mills for final grinding. Vibrating screens were close-circuited with the preliminary mill and the 18ft. air separator with the tube mills. The feed into one end of the ball mill was regulated by an "electric ear," which maintains by sound the optimum level of material in a mill through electric connection with the mill feeder, starting and stopping the feeder motor automatically. The material was discharged peripherally from the preliminary end of the mill and was passed equally over six 5ft. by 4ft. screens. A separation was made at 20-mesh; minus 20-mesh comprised the feed to the tube mills at the rate of 150 barrels per hour, and rejects were returned into the opposite end of the ball mill. The circulating load, with the screens, was 50 per cent.

The two tube mills, in simple circuit with the air separator, produced 90 barrels per hour each, with a circulating load of 50 per cent., and to a fineness of 1600 to 1800 sq. cm. per gramme surface area. This equalled the previous production with three mills and air separation, but the surface produced was much higher.

Early in 1942 the entire clinker grinding department was altered again. It now consists of two independent units, each with a new ball mill in closed circuit with screens, followed by the passage of minus 20-mesh material through a single tube mill in simple circuit with the 18ft. separator. The separator serves both

halves of the grinding plant. The capacity of each tube mill has been increased, as well as surface area, with a reduction in power consumption. Clinker is discharged directly from the rotary coolers on to a continuous carrier that fills 1,000 barrel bins over each preliminary mill. Dust gathered from the breechings ahead of the rotary coolers, where they are fed from the kilns, is collected and discharged continuously on to the carrier. Three 30-unit multiclone collectors were installed for the purpose. The preliminary mills are 9ft. diameter by 48in. ball mills, each driven through a magnetic clutch by a 250 h.p. synchronous motor. Each has automatic feed control, consisting of an " electric ear " which stops and starts a feedometer to regulate the flow of clinker from the bin to maintain the most efficient mill level.

Effect of Metal Sulphates on Rate of Hardening of Cement.

IN order to study the effect on the hardening of Portland cement concrete of various metal salts, independently of the effect of added anions, the following method has been devised by Mr. H. M. Larmour and W. F. Keyes, of the Yosemite Portland Cement Co.

A normal Portland cement clinker (not heat treated) was ground without gypsum to cement fineness. The sulphate of the metal under investigation was dissolved in the mixing water and the solution added to a mixture of sand, ground clinker and hydrated lime. The quantity of hydrated lime was that calculated as required to react with the metal sulphate to form metal hydroxide plus gypsum. The quantity of metal sulphate was such that the SO_3 equalled 1·5 per cent.

TABLE I

Metal sulphate addition and formula of compound	As metal oxide % by weight of cement	Compressive Strength (lb. per sq. in.)				
		Cured at 70 deg. F.			Cured at 110 deg. F.	
		3 days	7 days	28 days	7 days	28 days
Gypsum (no lime)	—	1,230	2,160	3,980	3,280	4,810
Aluminium $Al_2(SO_4)_3 18H_2O$ ..	0·64	1,530	2,670	4,110	4,460	4,880
Cobalt $CoSO_4 7H_2O$	1·41	1,460	2,450	3,510	3,650	3,960
Chromium $Cr_2(SO_4)_3 15H_2O$ ..	0·95	1,180	2,100	2,800	3,500	4,750
Copper $CuSO_4 5H_2O$	1·50	0	0	1,640	1,450	5,100
Iron (ic) $Fe_2(SO_4)_3 xH_2O$ ..	1·00	1,180	2,040	3,800	3,210	4,340
Iron(ous) $FeSO_4 7H_2O$ ..	1·35	680	2,040	3,660	3,310	4,860
Magnesium $MgSO_4 7H_2O$ ..	0·75	1,320	1,850	3,300	2,550	4,610
Manganese $MnSO_4 4H_2O$ ..	1·33	130	1,680	2,620	3,120	3,250
Nickel $NiSO_4 6H_2O$	1·40	1,350	1,880	3,240	2,910	4,780
Lead $PbSO_4$	4·18	0	1,600	2,930	2,860	4,580
Antimony $Sb_2(SO_4)_3$	1·82	1,480	3,310	3,470	3,800	4,640
Zinc $ZnSO_4 7H_2O$	1·52	0	1,560	2,880	0	4,940
None (with lime)	—	1,260	2,030	2,660	1,650	3,140
None (no lime)	—	1,080	1,750	—	2,180	—

by weight of cement (ground clinker, plus gypsum formed in the reaction). One part of cement, three parts of graded concrete sand passing the 8-mesh sieve, and a water-cement ratio of 0·9 were used. In each case the amount of water was corrected for the water of crystallisation of the metal sulphate and of gypsum. In the case of lead and antimony the sulphate was mixed with, rather than dissolved in, the water. The slump was determined with a 2-in. slump cone at the time of mixing and after fifteen minutes, thirty minutes, one hour, and two hours. The flow was determined on a flow table as described in Federal Specification SS-C-158-28. Slump results were entirely parallel.

Compressive test specimens were moulded in 2-in. by 4-in. paraffined cardboard cylinders for storage at 70 deg. F., 95 per cent. humidity, and in sealed 2-in. by 4-in. tin cans for storage at 110 deg. F. The specimens were capped with sulphur before testing. Compressive strength results are given in *Table* 1. It is believed that the amount of metal sulphate used (per cent. as metal oxide by weight of cement is given in *Table* 1) is greater than that likely to be encountered in any water or aggregates. It may be concluded that although the workability is reduced in practically every case from that obtained in the specimen containing added gypsum and no metal sulphate or hydrated lime, the deleterious effect on the strength is minimised at later ages and especially at higher curing temperatures.

The Cement and Concrete Association.

Mr. Halford W. L. Reddish, chairman and managing director of the Rugby Portland Cement Co., Ltd., has accepted the chairmanship of the Cement and Concrete Association for the third successive year.

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Additions to Portland Cement.

THE USE OF CATALYSTS.

AN account of recent investigations on the effect of admixtures on the properties of Portland cement, and some suggestions for future research, are given by Mr. Gabriel A. Ash, in a recent number of *Pit and Quarry*. In the course of his remarks the writer states that the composition of Portland cement lies within certain limits, however large fluctuations in the relationship of the principal oxides are admissible. Excellent hardening properties are produced by cements of high silica modulus; on the other hand, cements of low silica modulus show extraordinary properties too. The theoretical considerations regarding the constitution of Portland cement are based on the equilibria in the quaternary system CaO-Al_2O_3-SiO_2-Fe_2O_3 and the ternary system CaO-Al_2O_3-SiO_2. Due to the fact that the conditions of burning and cooling in the industry differ from those of the laboratory, there are some discrepancies between the theoretical conclusions and the reality of practice. The difference is caused by the fact that in commercial manufacturing the time of heating is very short and the conversion of CaO and C_2S to C_3S is incomplete. Complete combination occurs during sintering. In the last stage the equilibrium is frozen due to rapid cooling and resorption cannot occur, so that the flux forms a glass or crystallises independently. The latest investigations indicate that the amount of glass varies greatly with the different cooling rates. In slowly-cooled clinker it occurs infrequently. It has also been established that the agreement between phases calculated under the assumption of complete equilibrium crystallisation and the data of microscopic examination is better for slowly-cooled clinker.

The reactions between solid matters proceed very slowly. As Professor Jander pointed out, every reaction between solid matters depends not only on the surface conditions, but also on the interior structure and the energy contents of the reagents. These factors affect the speed of reaction and the character of structure of the newly-produced matter. This rule stands especially for the chemistry of Portland cement, since the silicates are characterised by their reaction inertia. Despite the fact that the ingredients are finely ground and intimately mixed, the reaction can take place at very high temperatures only. According to Lea and Desch, the silica of the lime-silica mixture is converted to dicalcium silicate at temperatures as high as 2,160 deg. F. The formation of tricalcium silicate in a mixture of sufficient lime content proceeds at 2,700 deg. F. The presence of alumina and ferric oxide in the lime-silica mixture favours the formation of tricalcium silicate at lower temperatures. It is unlikely, however, that C_3S could be formed at temperatures below 2,340 deg. F., because, according to Carlson, "it seems evident that C_3S is in a metastable state at temperatures below 2,340 deg. F., and that its tendency to dissociate reaches a maximum at about 2,100 deg. F." Thus the usual flame temperature in the cement kiln exceeds 2,500 deg. F. and flame temperatures even up to 2,800 deg. F. have been reported.

There are three factors producing perfect clinkering: the first is the temperature; the second is the time during which the ingredients are exposed to the maximum temperature; and the third is the rate of cooling. The time of exposure is very important. It is obvious that a general estimate of the time required cannot be made, for it depends on the properties of the raw materials and the system of the kilns as well. Considering, however, the fact that the formation of clinker within the kiln occurs when the exothermic reaction in the raw mix takes place, the time of exposure should be relatively short. Some experts give 20 minutes as an average time. The temperature of cement clinker, when discharged from a rotary kiln, ranges from 1,800 to 2,300 deg. F. Most cement makers emphasise the importance of " very rapid cooling," as the speed of cooling appears to have an important effect on the hardening properties of cement. The practical difficulties of an efficient cooling plant are still not completely overcome.

The perfect clinkering is a complicated and difficult process. It requires a very close control of burning conditions within the kiln and of the cooling of the clinker. In recent years this control of operations improved considerably due to the development in special apparatus and control devices. However, despite the remarkable improvements in the equipment of cement plants, there are still cases where peculiar properties of the raw materials are making perfect clinkering very difficult, if not impossible, and where, in order to arrive at a perfect clinkering, certain admixtures should be added to the available raw materials. The part played by such admixtures is not quite established. Not so long ago they were considered as fluxes lowering the melting point of the mixture. Now the opinion prevails that these matters act in manifold ways: as chemical agents taking part in the reaction with the ingredients of the primary mixture; as catalysts promoting the beginning of the exothermic reaction in the raw mix—the immediate forerunner of clinkering; or as so-called mineralisers.

Mineralisers are substances, small quantities of which are able to accelerate inertly proceeding reactions, favouring the formation of a state of equilibrium. According to Professor W. Eitel, " One of the most remarkable properties of mineralisers is the elimination of the tendency to glassy formation in certain systems of silicates. Thus, a mineraliser acts at the same time as a crystalliser." Professor Eitel's experiments show that calcium fluoride acts in this way. The admixture of fluorides reduces the viscosity of the melt. This effect appears to be especially energetic in the sintering reactions of cement clinker. In addition, fluorspar acts as a crystalliser. The ternary system CaO-CaF_2-$CaSiO_4$ shows an entecticum with CaO, CaF_2 and Beta C_2S as crystalline phases. The clinkering of raw meals blended with fluorspar shows that the glassy base crystallises completely, or nearly completely.

The effect of adding small amounts of certain materials to the raw mix in order to facilitate the clinkering has long been established. Cement manufacturers were rather reluctant to use such admixtures. The raw materials chosen for the production of Portland cement contain suitable fluxes in the form of alumina,

iron oxide, and alkalis. Only in relatively rare cases, when the raw materials were very difficult to burn, were fluxes, mostly fluorspar, used. Lately, however, ores containing iron and alumina were more frequently added to the raw material. The actual purpose was rather to readjust the composition of the raw mix than to facilitate the burning. In some cases better yield, or economy in fuel, has been, perhaps unintentionally, achieved.

According to the opinion of the majority of cement experts, such constituents of clinker as calcium aluminate and calcium-alumina ferrate develop so little strength that their presence is valueless as a strength-developing factor. For certain applications of cement the presence of tri-calcium aluminate is even harmful. An ideal hardening material would be a combination of high-limed silicates. Since the high-limed mixtures of lime and silica are very difficult to burn, the next problem is to find a suitable catalyst to make the commercial clinkering of such mixtures possible. Professor Ferrari partly solved the problem of clinkering high-limed mixtures in producing a cement composed of 75 per cent. C_3S and 25 per cent. C_4AF, using the minimum amount of sesquioxides and eliminating completely the existence of tricalcium aluminate. Comparison of this cement with other cements proved its superiority in all properties such as strength, shrinkage, elasticity, and resistance to aggressive solutions. This writer is convinced that the problems of producing commercial cements from high-limed silica mixes in the absence of sesquioxides, or in reducing their proportions to the minimum, can be completely solved.

In his studies on the system $CaO\text{-}CaF_2\text{-}CaSiO_4$ Professor Eitel found that the addition of CaF_2 was beneficial in promoting the formation of tricalcium silicate and in decreasing the clinkering temperature by 200 deg. C. This advantage of adding fluorspar was somewhat reduced by the fact that its presence accelerates the decomposition of C_3S at temperatures below 1,250 deg. C. and increases the rate of conversion of Beta C_2S to the Gamma form. However, this disadvantage can be partly eliminated by rapid cooling.

Very interesting results as to the mineralising effect of magnesia fluor-silicate on calcium-silica mixtures were recently published by Flint. The addition of 1 per cent. of $MgSiF_6$ proved to be effective. The comparison of samples of identical composition burned under the same conditions with and without adding magnesia fluor-silicate showed in the blended mixtures a considerable decrease of free lime and an increase of tricalcium silicate by from 20 to 30 per cent.

Professor Eitel sees the activating effect of the fluorides caused primarily by the attack of fluorine-ion on the silicates. The highly-polymerised network of the silicates is loosened by this attack. This disintegration results in the formation of complex ions SiF_4 and SiO_4. Both groups enter into exchange equilibrium in a manner similar to what we know it to be in a series of catalytically accelerating organic reactions. The loosening of the SiO_4-bond in the highly polymerised state, the creation of SiO_4 " islands " next to SiF_4 groups, the interchange of the anions and the thereafter following combination of the SiO_4 " islands" into a crystalline structure, comprise Professor Eitel's view of the linked-together

homogeneous reactions which characterise the mineralising and crystallising effect of a fluoride catalyst in a silicate system. Magnesia fluor-silicate is a cheap product, it is soluble in water, and can be easily added to the slurry. Contrary to the data published by other investigators, Flint's results prove the efficiency of $MgSiF_6$ as a catalyst.

Another problem is that of tricalcium silicate. The general opinion is that C_3A is an undesirable constituent. Numerous investigations apparently prove that its presence in cement causes the deterioration of concrete exposed to attacks of sulphate-solutions. Yet numerous structures made of cements containing considerable amounts of C_3A, made many years ago, still exist and do not show any signs of disintegration despite the presence of aggressive agents. There might be another reason for the vulnerability of certain cements to the attacks of aggressive solutions. The use of catalysts, such as a combination of fluorides, may result in the possibility of clinkering lime-silica mixtures without sesquioxides at all. The properties of such a cement might clarify the somewhat confused conception of the nature of C_3A.

The application of catalysts is certainly not limited to their use in raw mixes in order to facilitate the clinkering, or to improve the composition of the cement clinker. Various catalysts may find important application in influencing the setting and hardening of cement.

According to Dr. Forsén, during the hardening of Portland cement super-saturated solutions are formed and from these cement glue is separated. When the setting proceeds normally, the solubility of the aluminates is greatly diminished. In the case of quick setting, however, the aluminates dissolve rapidly. The retarders of the setting are compounds which decrease the solubility of the aluminates and produce the precipitation of a semi-permeable protective integument on the cement grains. The accelerators, like $CaCl_2$, decreasing the pH value of the reacting solutions, hasten the dissolving of the silicates and, by enriching the proportions of Ca-ions, promote the precipitation of calcium-silicate hydrate without an increase in the solubility of the aluminates. The destroyers of setting are compounds which, like sugar, borax, or humus, increase the solubility of the aluminates, forming reaction-products identical with those produced by quick-setting cements. Another type of destroyer is represented by compounds which, like phosphoric acid or fluorides, produce an insoluble skin on the cement grains. This indicates that a large field is open for the application of catalytic agents in order to modify or readjust the properties of clinker during or after grinding.

Preheater and Deheater for Rotary Lime Kilns.

WITH a view to increasing the efficiency of short rotary lime kilns, a stone preheater and a deheater for operation in conjunction with the kiln has been put on the market by the Kennedy-Van Saun Manufacturing and Engineering Corporation, of New York. It is claimed that the system increases the capacity of the kiln by 20 per cent. and effects a saving of fuel of 40 per cent. in some of the works in which it has been installed.

It is stated that the preheater heats stone of 60 to 80 deg. F. to temperatures of 1,250 deg. F. and higher before it enters the kiln. The comparatively short rotary-kiln section is then required only to heat the stone further to the calcination point and to complete this process. With the stone fed at a uniformly high temperature and utilisation of the heat from the combustion gases of controlled temperature from the lower end of the kiln, it is claimed very accurate control of calcination is possible. The deheater, which receives the calcinated material from the kiln, serves two purposes: the lime is " cured " in the " soaking-pit " section of the deheater and is then cooled before being discharged. Preheated air is also made available for combustion. In a typical installation crushed stone is introduced into the preheater through a combination feeder, which also acts as an air-seal. The bin storage is placed above the preheater if sufficient headroom is available.

The preheater consists of an insulated chamber with heat-resistant metal elements which bring the hot gases from the kiln into intimate contact with the raw stone in counterflow. This arrangement makes possible the maximum transfer of heat from the gases to the stone; the gases enter the deheater at temperatures of 1,250 to 1,600 deg. F. and leave it at 450 to 500 deg. F. The discharge mechanism at the bottom of the preheater regulates the withdrawal of stone so that all the stone receives the same treatment.

An appreciable amount of " pre-calcination " takes place in the preheater, reducing almost to final calcination the work done by the rotary-kiln section in which the stone is exposed to the combustion gases long enough for it to take up the required amount of heat but without overburning. The arrangement makes it possible to operate the kiln continuously at full capacity with the maximum transfer of heat, and the comparatively short kiln length keeps heat radiation losses low.

The calcined material is discharged from the rotary-kiln section into the deheater. This is another insulated chamber which is divided into two sections. About two hours are required for the burned lime to pass through the first, or " soaking-pit," section. During this period the hot lime is " cured " by its own latent heat and any underburned particles become completely calcined. In the second, or cooling, section of the deheater the lime is exposed to cooling air which in about 1½ hours lowers its temperature to about 200 deg. F. before it is discharged.

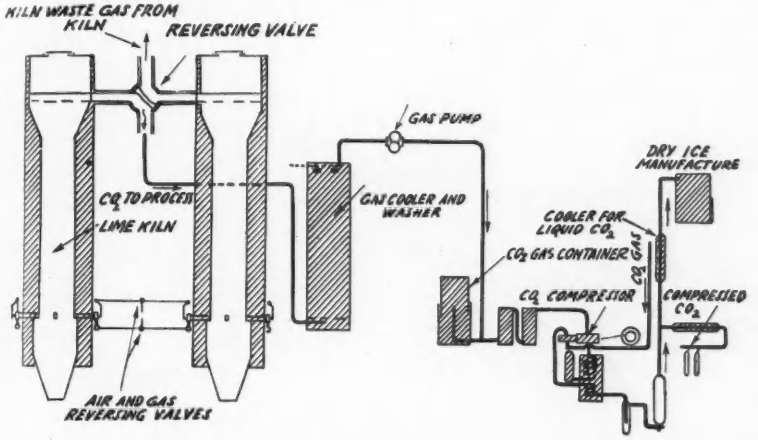
The application of heat to the stone is gradual up to the calcining point and the cooling rate follows an equally smooth downward curve. At no point is there a sharp increase or decrease of heat which might tend to crack or disintegrate the stone or the lime. This is important when the stone is very porous and contains considerable moisture. The material advances through the preheater into the kiln and through the deheater in a steady stream, while the bulk of the air enters the deheater at its discharge point and flows through the kiln and into and through the preheater in counterflow. This is in contrast with what happens in the ordinary rotary kiln, which subjects the cool raw stone to a sudden hot blast and which often drops the hot lime into a chilling blast of cool air with damaging effect on the structure of each lump of lime. The mechanical friction and breakage in the system is also much less. The hot stone entering the rotary section deposits an even coating of lime on the firebrick from the feed end to the calcining zone. This coating becomes glazed and absorbs much of the wear usually borne by the refractories. The removal of dust in the preheater is chiefly responsible for the decrease in ring formation.

The deheater makes possible the operation of the kiln so that lime may be deliberately underburned and its calcination completed in the soaking-pit section by the latent heat of the burned lime. The lime thus produced contains the minimum number of cores due to underburning, and the minimum of discoloration and poor-quality lime due to overburning.

Tests were made on a 7 ft. 6 in. by 125-ft. rotary kiln with preheater and deheater designed for a capacity of 125 tons of lime in 24 hours; an output of 75 to 100 tons daily is all that is required at present. The guaranteed fuel consumption was 6,000,000 B.T.U. per ton of lime, and this figure was already exceeded when an output of only 100 tons daily was reached. At 110 tons capacity, the maximum obtainable with present storage and handling facilities, the average fuel consumption was 5,600,000 B.T.U. per ton. A stone ranging from dust up to 2 in. was used instead of the smaller and more uniform stone generally used. The use of an exhauster fan made it possible to keep a well-balanced condition in the firing-hood. A plus-minus zero pressure was maintained with a combustion gas of $\frac{3}{4}$ per cent. oxygen to 1 per cent. carbon monoxide. The use of *louvre* dampers made accurate air control possible. The hot air coming from the deheater contained 4 per cent. CO_2, which was a good indication of after-calcination. The kiln is fired with 1,080-B.T.U. natural gas. A potentiometer recorder records the temperature of the lining after it had left the lime bed; this recorder immediately indicated any minor change in the air, gas or draught, and made it easy to get the most heat out of the best combination. The high-calcium limestone used contains 54 per cent. CaO, 0·5 per cent. MgO, and 42·8 per cent. CO_2. After being crushed and screened, it is stored in three bins. During the period when the tests were made the stone contained about 3 per cent. of moisture. Capacity was measured on the lime conveyor after running from 16 to 24 hours.

Carbon Dioxide from Lime Kilns.

IN the course of a discussion on efficient ways of arranging lime kilns for the recovery of concentrated CO_2 without absorption systems, Mr. V. J. Azbe states in a recent number of "Rock Products" that with high calcium limestone being almost half CO_2 and dolomitic stone even more than half, it seems that the lime kiln should be about as good a source of CO_2 as any, but, except for alkali and sugar manufacturing plants, there is seldom any effort made at its recovery and utilisation. Two lime plants producing precipitated chalk are known to produce CO_2 for the process separately in coke furnaces rather than recover it from kilns. A plant where CO_2 is absorbed from lime-kiln gases is an exception, but in one such case low-strength gas of about 20 per cent. CO_2 is recorded, while this paper deals with the recovery of gas of nearly 100 per cent. CO_2.



Arrangement of Two Kilns Fired Alternately, with Shut-off to Prevent Access of Air, to Extend the Period of Evolution of CO_2.

Random tapping of a lime kiln may produce a moisture saturated and corrosive gas, containing at times possibly even less than 15 per cent. CO_2, which for many reasons may prove so troublesome as to be worthless. It is not difficult to work out an arrangement so that dry kiln gases would be obtained with CO_2 even in excess of 30 per cent. Such a gas could be used in some processes directly, but in most cases the CO_2 would still be too low and the whole would have to pass through a process of absorption by solutions and subsequent boiling off to give the desired concentration of nearly 100 per cent. CO_2.

Processes for obtaining this high concentration without the use of an absorption system involve indirect heating of limestone through walls similar to those in calcining retorts, except that the retorts are large and arranged for continuous operation. Calcination of lime is a high-

temperature operation and the transfer of great amounts of high heat through walls, to avoid mixing the products of combustion with CO_2 from the stone, presents serious problems of design and operation. First cost and operating costs can readily defeat the advantages that there may be over the conventional system when gases low in CO_2 are concentrated by absorption.

In view of the fact that the demand for CO_2 may increase due to its use in manufacturing synthetic rubber, it seems advisable to call attention to a system of obtaining high strength CO_2 (U.S. Patent No. 2199384) which is closely related to ordinary lime-plant practice and which utilises kilns very much like the ordinary kiln of the more modern design. A lime kiln that is well heated and producing lime at a good rate has a great deal of stored heat. If, on such a kiln, either the natural gas were shut off, or the grates drawn bare of fire, or the producer gas closed off, the kiln would still continue to make lime at a progressively slower rate for an hour or so longer and would continue to pass off CO_2 gas. This can be readily proved on almost any lime kiln with a simple Orsat apparatus.

If a kiln were arranged so that it could be shut off against the access of air, the heat in the kiln would be retained longer and the CO_2 evolving period extended. The kiln then would become virtually an internally-heated retort and the gas coming off, being undiluted with air or products of combustion, would be practically pure CO_2 gas. Such a gas, after cooling, could be compressed, liquified, solidified, or otherwise treated without passing it through the usual chemical absorption processes. The illustration shows the more essential features of this system arranged for continuous operation with two kilns fired alternately. If natural gas were the fuel, one kiln supplemented with a substantial gasometer would be suitable.

Electrical methods of retorting limestone are too expensive to be practical. There is not only the matter of conversion of limestone into lime to be considered, which requires a great deal of heat, but the preheating of the limestone, radiation losses and, in addition, sensible heat would not be recoverable. Electrical heating could, however, be used in conjunction with this kiln in a supplementary manner during the retorting period in which the CO_2 is driven off. This optional use of electricity would lengthen the period during which the CO_2 would be given off. During the period of heating up the kiln the electricity would be off, while the normal processes of stone preheating, of lime cooling and drawing, and of heating up the charge and off-walls would take place. It would only be used during the period when pure CO_2 would be generated, and so for every kilowatt-hour of energy $2\frac{1}{2}$ lb. of lime and 2 lb. of additional CO_2 gas would be given off. The electric heating elements would be placed below where the combustion process would take place and so out of the high heat which might damage them.

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